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2,3-Dichloro-5,8-dimethoxy-1,4-naphthoquinone

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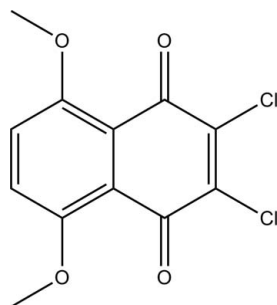
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Key indicators: single-crystal X-ray study; $T = 123$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.028; wR factor = 0.077; data-to-parameter ratio = 13.2.

In the crystal structure of the title compound, $\text{C}_{12}\text{H}_8\text{Cl}_2\text{O}_4$, molecules crystallize in planes parallel to $(\bar{2}04)$ with an interplanar distance of 3.288 (2) Å [centroid-centroid distance = 3.819 (2) and slippage = 1.932 (2) Å]. The structure features $\text{C}-\text{H}\cdots\text{O}$ interactions involving methoxy and aromatic H atoms and the carbonyl O atoms as well as a $\text{C}-\text{H}\cdots\text{Cl}$ interaction involving an aromatic H atom. In addition there are short interhalogen contacts between adjoining molecules [$\text{Cl}\cdots\text{Cl} = 3.3709$ (5) Å].

Related literature

For biological properties of the title compound, see: Huang *et al.* (1998); Copeland *et al.* (2007); Lien *et al.* (1997). For structures of related 2,3-dichloro-1,4-naphthoquinone derivatives, see: Ikemoto *et al.* (1977); Rubio *et al.* (1985). For quinoid systems, see: Driebergen *et al.* (1986); Scheuermann *et al.* (2009).



Experimental

Crystal data

$\text{C}_{12}\text{H}_8\text{Cl}_2\text{O}_4$
 $M_r = 287.08$
 Monoclinic, $C2/c$
 $a = 9.9366$ (2) Å

$b = 15.6564$ (3) Å
 $c = 14.8505$ (3) Å
 $\beta = 103.782$ (2)°
 $V = 2243.79$ (8) Å³

$Z = 8$
 Cu $K\alpha$ radiation
 $\mu = 5.27$ mm⁻¹

$T = 123$ K
 $0.81 \times 0.30 \times 0.23$ mm

Data collection

Oxford Diffraction Xcalibur Ruby Gemini diffractometer
 Absorption correction: analytical (*CrysAlis PRO*; Oxford Diffraction, 2007)
 $T_{\min} = 0.154$, $T_{\max} = 0.418$
 8037 measured reflections
 2199 independent reflections
 2156 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.077$
 $S = 1.09$
 2199 reflections

166 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C7}-\text{H7A}\cdots\text{Cl2}^i$	0.95	2.72	3.6593 (14)	169
$\text{C8}-\text{H8A}\cdots\text{O2}^i$	0.95	2.54	3.3337 (18)	142
$\text{C11}-\text{H11C}\cdots\text{O1}^{ii}$	0.98	2.62	3.4030 (19)	137
$\text{C12}-\text{H12A}\cdots\text{O1}^{iii}$	0.98	2.49	3.3723 (19)	149

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 1, y, -z + \frac{3}{2}$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2007); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5932).

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supplementary materials

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2,3-Dichloro-5,8-dimethoxy-1,4-naphthoquinone

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Comment

Compounds with the methoxy and chloro groups on the 1,4-naphthoquinone skeleton were reported to show inhibitory effects on cancerous cells (Huang *et al.*, 1998; Lien *et al.*, 1997). 2,3-Dichloro-5,8-dimethoxy-1,4-naphthoquinone, C₁₂H₈Cl₂O₄, was synthesized as a potential anticancer agent and has been reported to exhibit anti-inflammatory, antiplatelet, anti-allergic and anticancer activities (Huang *et al.*, 1998; Copeland *et al.*, 2007). This biological function is based on chemical properties inherent in molecule. To understand its biological behavior, therefore, it is of great importance to determine the structural property and its molecular dimensions. The methoxy and chloro group in the quinoid ring give it interesting redox and biological properties as well as an excellent coordination site (Driebergen *et al.*, 1986; Scheuermann *et al.*, 2009). The coordinating potential of the molecule could be used as a tool for the formation of new organometallic compounds (Scheuermann *et al.*, 2009).

The molecules in the title compound crystallize in planes parallel to (-2 0 4) with an interplanar distance of 3.288 Å forming a charge transfer complex. The distance between the overlapping planes of neighboring molecules is 3.385 (3) Å and 3.653 (3) Å. There are intermolecular interactions between both a methoxy hydrogen and an aromatic hydrogen and the carbonyl O atoms. Intermolecular interactions are also observed between chlorine atom and the aromatic and methoxy H atoms. In addition there are short interhalogen contacts between adjoining molecules (C11...Cl2 3.3709 (5) Å) These C—H...Cl, C—H...O and Cl...Cl interactions in the crystal structure link the molecules to produce a three dimensional network.

Experimental

2,3-Dichloro-5,8-dimethoxy-1,4-naphthoquinone (DDNQ) was synthesized as described by Huang (Huang *et al.*, 1998). The reaction of dichloromaleic anhydride and 1,4-dimethoxybenzene produces a mixture of 6,7-dichloro-5,8-dihydroxy-1,4-naphthoquinone and 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone. *o*-Methylation of 6,7-dichloro-5,8-dihydroxy-1,4-naphthoquinone and 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone with methyl iodide-silver oxide produces the mixture of 6,7-dichloro-5,8-dimethoxy-1,4-naphthoquinone (1) and 2,3-dichloro-5,8-dimethoxy-1,4-naphthoquinone (2). The mixture of 1 and 2 were separated by column chromatography on silica gel to obtain pure 2,3-dichloro-5,8-dimethoxy-1,4-naphthoquinone (DDNQ). Solid DDNQ was recrystallized in dichloromethane to produce X-ray diffraction quality crystals.

Refinement

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with a C—H distance of 0.95 Å $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and 0.98 Å for CH₃ [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$].

Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2007); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2007); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

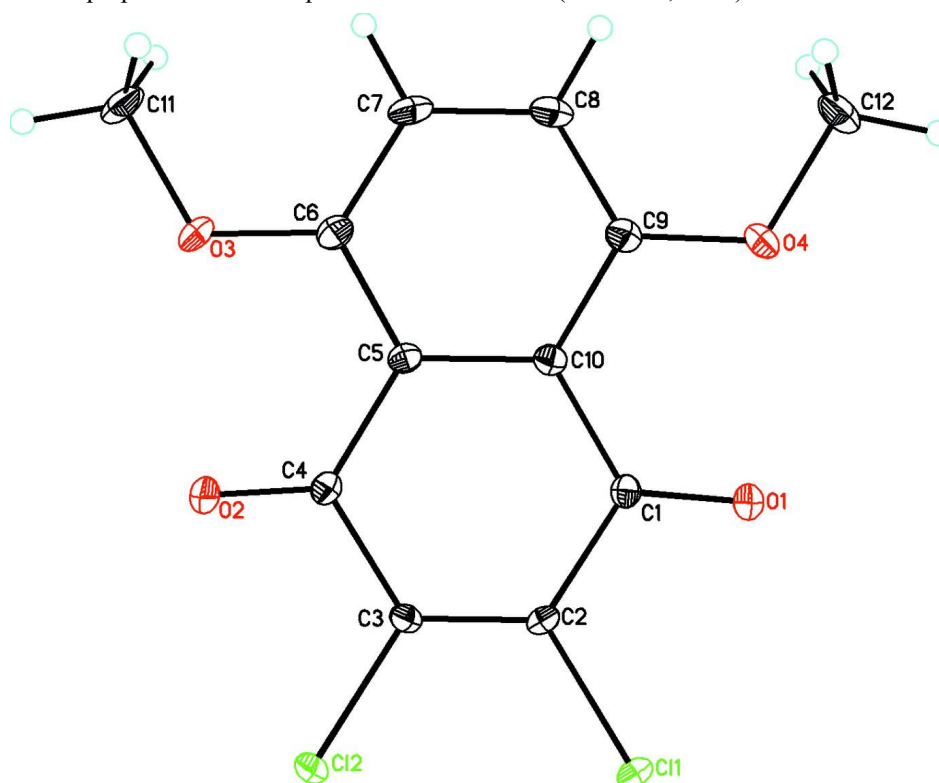


Figure 1

Diagram of $C_{12}H_8Cl_2O_4$ with atomic displacement parameters drawn at 30% probability.

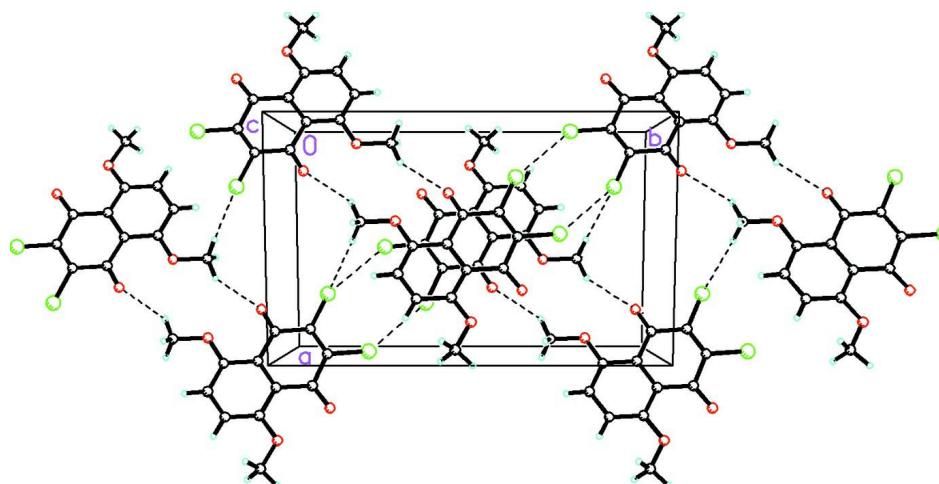


Figure 2

The molecular packing for $C_{12}H_8Cl_2O_4$ viewed along the *c* axis.

2,3-Dichloro-5,8-dimethoxy-1,4-naphthoquinone

Crystal data

$C_{12}H_8Cl_2O_4$	$F(000) = 1168$
$M_r = 287.08$	$D_x = 1.700 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
Hall symbol: $-C 2yc$	Cell parameters from 6065 reflections
$a = 9.9366 (2) \text{ \AA}$	$\theta = 3.1\text{--}72.4^\circ$
$b = 15.6564 (3) \text{ \AA}$	$\mu = 5.27 \text{ mm}^{-1}$
$c = 14.8505 (3) \text{ \AA}$	$T = 123 \text{ K}$
$\beta = 103.782 (2)^\circ$	Slab, pink
$V = 2243.79 (8) \text{ \AA}^3$	$0.81 \times 0.30 \times 0.23 \text{ mm}$
$Z = 8$	

Data collection

Oxford Diffraction Xcalibur Ruby Gemini diffractometer	8037 measured reflections
Radiation source: Enhance (Cu) X-ray Source	2199 independent reflections
Graphite monochromator	2156 reflections with $I > 2\sigma(I)$
Detector resolution: $10.5081 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.024$
ω scans	$\theta_{\text{max}} = 72.5^\circ$, $\theta_{\text{min}} = 5.4^\circ$
Absorption correction: analytical	$h = -12 \rightarrow 12$
(<i>CrysAlis PRO</i> ; Oxford Diffraction, 2007)	$k = -19 \rightarrow 18$
$T_{\text{min}} = 0.154$, $T_{\text{max}} = 0.418$	$l = -13 \rightarrow 18$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.028$	$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 1.7012P]$
$wR(F^2) = 0.077$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{\text{max}} = 0.001$
2199 reflections	$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
166 parameters	$\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$
0 restraints	Extinction correction: <i>SHELXL</i> ,
Primary atom site location: structure-invariant direct methods	$Fc^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.00077 (11)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.22986 (3)	0.61933 (2)	0.50894 (2)	0.02353 (13)
Cl2	0.47240 (4)	0.73207 (2)	0.62182 (2)	0.02670 (14)

O1	0.29765 (11)	0.44185 (6)	0.51438 (7)	0.0247 (2)
O2	0.70729 (11)	0.63328 (7)	0.71429 (7)	0.0256 (2)
O3	0.83562 (11)	0.50132 (7)	0.79392 (7)	0.0266 (3)
O4	0.41728 (11)	0.30361 (6)	0.58176 (7)	0.0246 (2)
C1	0.39013 (13)	0.48023 (9)	0.56736 (9)	0.0163 (3)
C2	0.37962 (13)	0.57504 (9)	0.57239 (9)	0.0163 (3)
C3	0.48343 (14)	0.62303 (8)	0.62041 (9)	0.0169 (3)
C4	0.61546 (13)	0.58551 (9)	0.67577 (9)	0.0166 (3)
C5	0.62262 (13)	0.49062 (9)	0.68126 (9)	0.0160 (3)
C6	0.73632 (14)	0.45098 (9)	0.74118 (9)	0.0194 (3)
C7	0.74226 (15)	0.36157 (10)	0.74499 (10)	0.0233 (3)
H7A	0.8192	0.3346	0.7852	0.028*
C8	0.63901 (16)	0.31218 (9)	0.69163 (10)	0.0232 (3)
H8A	0.6467	0.2517	0.6946	0.028*
C9	0.52280 (15)	0.34971 (9)	0.63305 (10)	0.0193 (3)
C10	0.51411 (14)	0.43964 (9)	0.62756 (9)	0.0162 (3)
C11	0.94626 (15)	0.46147 (11)	0.86031 (11)	0.0291 (3)
H11A	1.0087	0.5054	0.8939	0.044*
H11B	0.9978	0.4235	0.8282	0.044*
H11C	0.9079	0.4282	0.9042	0.044*
C12	0.42089 (18)	0.21201 (9)	0.59175 (12)	0.0295 (3)
H12A	0.3370	0.1873	0.5518	0.044*
H12B	0.4255	0.1970	0.6565	0.044*
H12C	0.5027	0.1894	0.5737	0.044*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.01650 (19)	0.0218 (2)	0.0275 (2)	0.00482 (11)	-0.00425 (14)	0.00124 (12)
C12	0.0297 (2)	0.01223 (19)	0.0314 (2)	0.00149 (12)	-0.00606 (15)	-0.00074 (12)
O1	0.0218 (5)	0.0195 (5)	0.0281 (5)	-0.0027 (4)	-0.0033 (4)	-0.0024 (4)
O2	0.0204 (5)	0.0211 (5)	0.0300 (6)	-0.0041 (4)	-0.0045 (4)	-0.0011 (4)
O3	0.0190 (5)	0.0279 (6)	0.0263 (5)	0.0043 (4)	-0.0075 (4)	0.0011 (4)
O4	0.0260 (5)	0.0131 (5)	0.0331 (6)	-0.0016 (4)	0.0036 (4)	-0.0014 (4)
C1	0.0152 (6)	0.0171 (7)	0.0167 (6)	-0.0015 (5)	0.0041 (5)	-0.0003 (5)
C2	0.0131 (6)	0.0182 (7)	0.0163 (6)	0.0032 (5)	0.0009 (5)	0.0019 (5)
C3	0.0194 (7)	0.0124 (7)	0.0182 (7)	0.0012 (5)	0.0030 (5)	0.0004 (5)
C4	0.0156 (6)	0.0192 (7)	0.0146 (6)	-0.0003 (5)	0.0024 (5)	0.0004 (5)
C5	0.0146 (6)	0.0173 (7)	0.0164 (6)	0.0024 (5)	0.0041 (5)	0.0015 (5)
C6	0.0165 (6)	0.0238 (7)	0.0181 (7)	0.0029 (5)	0.0042 (5)	0.0014 (5)
C7	0.0196 (7)	0.0248 (7)	0.0256 (7)	0.0093 (6)	0.0055 (6)	0.0090 (6)
C8	0.0244 (7)	0.0172 (7)	0.0298 (8)	0.0050 (5)	0.0104 (6)	0.0059 (6)
C9	0.0201 (7)	0.0177 (7)	0.0214 (7)	0.0006 (5)	0.0076 (5)	0.0009 (5)
C10	0.0168 (6)	0.0155 (7)	0.0172 (6)	0.0011 (5)	0.0057 (5)	0.0010 (5)
C11	0.0202 (7)	0.0375 (9)	0.0244 (7)	0.0104 (6)	-0.0050 (6)	0.0029 (6)
C12	0.0359 (9)	0.0140 (7)	0.0406 (9)	-0.0018 (6)	0.0129 (7)	-0.0020 (6)

Geometric parameters (Å, °)

C11—C2	1.7074 (13)	C5—C10	1.4233 (19)
C12—C3	1.7111 (13)	C6—C7	1.402 (2)
O1—C1	1.2166 (17)	C7—C8	1.375 (2)
O2—C4	1.2126 (17)	C7—H7A	0.9500
O3—C6	1.3564 (18)	C8—C9	1.399 (2)
O3—C11	1.4331 (17)	C8—H8A	0.9500
O4—C9	1.3492 (18)	C9—C10	1.4117 (18)
O4—C12	1.4413 (17)	C11—H11A	0.9800
C1—C10	1.4819 (19)	C11—H11B	0.9800
C1—C2	1.4911 (18)	C11—H11C	0.9800
C2—C3	1.3367 (19)	C12—H12A	0.9800
C3—C4	1.4927 (18)	C12—H12B	0.9800
C4—C5	1.4886 (18)	C12—H12C	0.9800
C5—C6	1.4052 (19)		
C6—O3—C11	118.53 (12)	C6—C7—H7A	119.3
C9—O4—C12	118.51 (12)	C7—C8—C9	120.94 (13)
O1—C1—C10	124.72 (13)	C7—C8—H8A	119.5
O1—C1—C2	118.22 (12)	C9—C8—H8A	119.5
C10—C1—C2	117.05 (11)	O4—C9—C8	122.80 (13)
C3—C2—C1	122.14 (12)	O4—C9—C10	118.19 (12)
C3—C2—C11	121.77 (11)	C8—C9—C10	119.00 (13)
C1—C2—C11	116.03 (10)	C9—C10—C5	119.95 (12)
C2—C3—C4	122.54 (12)	C9—C10—C1	119.55 (12)
C2—C3—C12	121.59 (11)	C5—C10—C1	120.49 (12)
C4—C3—C12	115.87 (10)	O3—C11—H11A	109.5
O2—C4—C5	124.68 (12)	O3—C11—H11B	109.5
O2—C4—C3	118.74 (12)	H11A—C11—H11B	109.5
C5—C4—C3	116.56 (11)	O3—C11—H11C	109.5
C6—C5—C10	119.64 (13)	H11A—C11—H11C	109.5
C6—C5—C4	119.75 (12)	H11B—C11—H11C	109.5
C10—C5—C4	120.60 (12)	O4—C12—H12A	109.5
O3—C6—C7	122.63 (13)	O4—C12—H12B	109.5
O3—C6—C5	118.27 (13)	H12A—C12—H12B	109.5
C7—C6—C5	119.10 (13)	O4—C12—H12C	109.5
C8—C7—C6	121.33 (13)	H12A—C12—H12C	109.5
C8—C7—H7A	119.3	H12B—C12—H12C	109.5
O1—C1—C2—C3	-172.16 (13)	C4—C5—C6—C7	-179.42 (12)
C10—C1—C2—C3	7.53 (19)	O3—C6—C7—C8	179.06 (13)
O1—C1—C2—C11	5.05 (16)	C5—C6—C7—C8	-0.2 (2)
C10—C1—C2—C11	-175.27 (9)	C6—C7—C8—C9	-1.4 (2)
C1—C2—C3—C4	-2.5 (2)	C12—O4—C9—C8	3.6 (2)
C11—C2—C3—C4	-179.59 (10)	C12—O4—C9—C10	-175.82 (12)
C1—C2—C3—C12	177.39 (10)	C7—C8—C9—O4	-177.91 (13)
C11—C2—C3—C12	0.34 (17)	C7—C8—C9—C10	1.5 (2)
C2—C3—C4—O2	176.86 (13)	O4—C9—C10—C5	179.39 (12)
C12—C3—C4—O2	-3.09 (17)	C8—C9—C10—C5	-0.06 (19)

C2—C3—C4—C5	-4.63 (19)	O4—C9—C10—C1	0.79 (18)
C12—C3—C4—C5	175.42 (9)	C8—C9—C10—C1	-178.66 (12)
O2—C4—C5—C6	6.3 (2)	C6—C5—C10—C9	-1.52 (19)
C3—C4—C5—C6	-172.15 (12)	C4—C5—C10—C9	179.58 (11)
O2—C4—C5—C10	-174.84 (13)	C6—C5—C10—C1	177.06 (11)
C3—C4—C5—C10	6.75 (18)	C4—C5—C10—C1	-1.83 (18)
C11—O3—C6—C7	-4.1 (2)	O1—C1—C10—C9	-6.9 (2)
C11—O3—C6—C5	175.23 (12)	C2—C1—C10—C9	173.40 (11)
C10—C5—C6—O3	-177.66 (12)	O1—C1—C10—C5	174.48 (12)
C4—C5—C6—O3	1.24 (18)	C2—C1—C10—C5	-5.19 (18)
C10—C5—C6—C7	1.67 (19)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C7—H7 <i>A</i> ...C12 ⁱ	0.95	2.72	3.6593 (14)	169
C8—H8 <i>A</i> ...O2 ⁱ	0.95	2.54	3.3337 (18)	142
C11—H11 <i>C</i> ...O1 ⁱⁱ	0.98	2.62	3.4030 (19)	137
C12—H12 <i>A</i> ...O1 ⁱⁱⁱ	0.98	2.49	3.3723 (19)	149

Symmetry codes: (i) $-x+3/2, y-1/2, -z+3/2$; (ii) $-x+1, y, -z+3/2$; (iii) $-x+1/2, -y+1/2, -z+1$.